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Title: **EP0623569B1: Ceramic composition thermistor element comprising and processes for producing same**[German][French]

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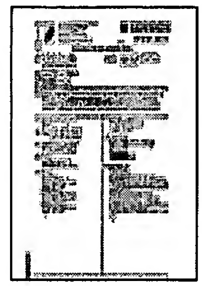

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Abstract: [From equivalent EP0623569A1] A ceramic composition especially useful for a thermistor exhibiting stable resistance values over a wide temperature range and capable of being used for a prolonged time is described. The composition is represented by the formula (M1MýO2)1-x ú (M1AlO3)x, wherein M1 is an element selected from the elements of the group 3A excluding La and Mý is an element of the groups 4A, 5A, 6A, 7A and 8, and wherein the mixing ratio between an electrically conductive substance stable at elevated temperatures and an insulating substance stable at elevated temperatures, may be adjusted. A thermistor formed of the composition is superior in high-temperature stability and can be used over a broad temperature range because its resistance value can be selected to an optimum value. Furthermore described is a process for producing a ceramic composition and a process for producing a thermistor element (1).

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Designated Country: DE FR

Family: Show known family members (at least 8)

Description: Expand full description

First Claim: Show all claims

1. A ceramic composition represented by the formula $(M^1M^2O_3)_{1-x} \cdot (M^1AlO_3)_x$, where

- M^1 is one or more elements selected from the elements belonging to the group 3A excluding La, M^2 is one or more elements selected from the elements belonging to the groups 4A, 5A, 6A, 7A and 8, and $0.8>x>0$, preferably $x \geq 0.01$.
  [German] [French]

Forward References: Go to Result Set: Forward references (2)

PDF	Patent	Pub.Date	Inventor	Assignee	Title
	US6306315	2001-10-23	Ogata; Itsuhei	Denso Corporation	Thermistor device thermistor manufacturing method and te sensor
	US5879750	1999-03-09	Kuzuoka; Kaoru	Denso Corporation	Method for manufacturing the materials and thermistors

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(54) Ceramic composition thermistor element comprising same, and processes for producing same

Keramische Zusammensetzung, Thermistor Teil daraus sowie Verfahren zu ihrer Herstellung

Composition céramique, élément thermistor ayant cette composition, et procédé sa fabrication

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- **"Taschenbuch der Physik", H.Kuchling,6. Auflage (1984), Verlag Harri Deutsch/Thun und Frankfurt/Main; pages 396_397.**
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Description

[0001] This invention relates to a ceramic (or porcelain) composition for a thermistor, a thermistor element comprising the ceramic composition as well as processes for producing the ceramic composition and the thermistor element.

[0002] As a thermistor material which may be employed at higher temperatures, (a) a material mainly composed of a corundum type crystal structure, as disclosed for example in JP Patent KOKAI Publication No. 50-118294 (JP-A-118294/75) or in "Fine Ceramic Handbook" by K. Yano, published by ASAKURA SHOTEN in 1984; (b) a material mainly composed of a compound having a spinel type crystal structure, as disclosed for example in JP Patent KOKAI Publication No. 49-63995 (JP-A-63995/74), (c) a material mainly composed of zirconia, as disclosed in e.g. "Nainenkikan" (Internal Combustion Engine) vol 30, No. 8, page 98, and (d) a material mainly composed of a compound having a perovskite type crystal structure, may be used. US-A-4 229 322 discloses a ceramic component suitable for preparing electrodes having the compositional formula:

$$Y_x(Mg_y\, Cr_z)_w\, Al_{(1\text{-}w)}\, O_3.$$

[0003] Furthermore, JP-A-51 108 298 describes a resistance ceramic composition used in thermistors comprising $LaCrO_3$ and $LaAlO_3$.

[0004] However, according to the eager investigation of the inventors of the present invention the following problems have been turned out. With the material (a) mainly composed of the corundum crystal structure, the resistance - temperature characteristics cannot be adjusted to a larger extent. If, for example, the additive is added in an excess quantity, the structure ceases to remain the stable corundum type crystal structure, resulting in deteriorated thermal stability.

[0005] The material (b) mainly composed of the spinel type crystal structure has a higher rate of change of the resistance versus temperature (a higher temperature gradient constant β), so that it cannot be employed over a wider temperature range. On the other hand, materials mainly composed of $NiAl_2O_4$ or $CoAl_2O_4$ are low in the thermal resistance and hence cannot be employed at elevated temperatures.

[0006] The material (c) mainly composed of zirconia is oxygen ion conductive and is increased in resistance in a temperature range lower than the activation temperature so that it cannot be employed practically.

[0007] The material (d) mainly composed of the compound having the perovskite type crystal structure has such inconvenience that, if only a slight amount of La oxides remain unreacted, the non-reacted La component reacts with the atmospheric moisture to form unstable $La(OH)_3$ with the result that the device composed of the material collapses or exhibits only unstable resistance values.

[0008] It is therefore the object of the present invention to provide an improved novel ceramic composition and an improved thermistor element comprising the ceramic composition which avoid the above mentioned drawbacks. This object is solved by the composition according to independent claim 1, the thermistor element according to independent claim 10, the process for producing a ceramic composition according to independent claim 11, and the process for producing a thermistor element according to independent claim 19. Further advantageous features, aspects and details of the invention are evident from the dependent claims, the description, the examples and the drawings.

[0009] The present invention provides a ceramic thermistor which overcomes the above problems.

[0010] It is a further aspect of the present invention to provide a ceramic composition especially useful as a base material for a thermistor which has a broad range of resistance values by adjusting the composition of the material.

[0011] It is still a further aspect of the present invention to provide a ceramic composition for thermistor which can be sintered at a temperature not higher than 1600°C to prevent electrode deterioration, which is free from hygroscopic substances and the resulting sintered body is less susceptible to deterioration in characteristics due to the atmospheric humidity or heat hysteresis and which can be employed over a wide temperature range of from room temperature to 1100°C.

[0012] According to another aspect, the present invention provides a composition for a thermistor, which is superior in high temperature stability.

[0013] It is a further aspect of the present invention to provide not only the ceramic compositions aforementioned, but to provide an improved thermistor elements which are obtainable by sintering the aforesaid compositions.

[0014] It is also an aspect of the present invention to provide a process for producing the aforementioned compositions and thermistor element using the same.

[0015] Still further aspects of the invention will become apparent from the entire disclosure.

[0016] At least one of the said aspects is accomplished by the following ceramic composition and a thermistor element obtainable from this composition. The present invention further provides a process for producing a thermistor element.

[0017] The ceramic composition for the thermistor according to the present invention especially useful for the production of a thermistor is represented by the formula $(M^1M^2O_3)_{1\text{-}x}\cdot(M^1AlO_3)_x$, where

M^1 is one or more elements selected from the elements belonging to the group 3A excluding La, M^2 is one or more elements selected from the elements belonging to the groups 4A, 5A, 6A, 7A and 8 and 0.8>x>0.

[0018] Part of the elements may be inter-diffused with each other, such as is the case with certain element(s) of M^2 and Al.

Definition:

[0019] The groups 3A, 4A, 5A, 6A and 7A herein mean 3A, 4A, 5A, 6A and 7A of the Periodic Table according to the agreement in 1965 of the Committee for the Nomenclature for Inorganic Chemistry of International Union of Pure and Applied Chemistry (IUPAC).

[0020] According to the process aspect of the present invention, there is provided a process for producing a composition for thermistor comprising:

providing $M^1M^2O_3$ and M^1AlO_3, respectively, where M^1 is one or more elements selected from the elements belonging to the group 3A excluding La, M^2 is one or more elements selected from the elements belonging to the groups 4A, 5A, 6A, 7A and 8, and
then providing a mixture comprising $(M^1M^2O_3)_{1-x} \cdot (M^1AlO_3)_x$ where 0.8>x>0.

PREFERRED EMBODIMENTS

[0021] The ceramic composition for a thermistor represented by $(M^1M^2O_3)_{1-x} \cdot (M^1AlO_3)_x$, where M^1 is one or more elements selected from the elements Y, Sm, Pr, Nd, Dy, Ho, Er, Gd and Yb and/or M^2 is one or more elements selected from the elements Cr, Ti, Mn, Fe and Co, where 0.8>x>0, does not exhibit hygroscopicity, is free from deterioration in strength and superior in thermal resistance. The preferred value of x is 0.01 or more for an effective roll of x.

[0022] A preferred ceramic composition for a thermistor with x being 0.05 to 0.5 also does not exhibit hygroscopicity and is free from deterioration in strength and superior in thermal resistance, so that it can be adjusted to practically satisfactory resistance values. The most preferred values of x are 0.1 - 0.4.

[0023] The ceramic composition for a thermistor mainly composed of a composition comprising $(M^1M^2O_3)_{1-x} \cdot (M^1AlO_3)_x$ admixed with a sintering aid (or aids) for improving sinterability exhibits high strength and superior thermal resistance. Any sintering aid capable of forming a liquid phase in the grain boundary for improving sinterability of the ceramics suffices. silica, mullite or the like is preferred. The amount of addition of the sintering aid is 0.5 to 10 wt% and preferably ranges between 0.8 to 5 wt%.

[0024] $M^1M^2O_3$ is a substance exhibiting higher electrical conductivity and M^1AlO_3 is a substance exhibiting lower electrical conductivity. A thermistor may be provided in which, by changing the mixing ratio of these two substances, the resistance values can be easily changed and may be maintained stably at higher temperatures. The reason why the thermistor exhibits superior stability at elevated temperatures is presumably that such substances as $M^1M^2O_3$ or M^1AlO_3 are stable at elevated temperatures, and that the melting points of $YCrO_3$ and $YAlO_3$ compounds, for example, are as high as approximately 2300°C and 1900°C, respectively.

[0025] It has been found that a mixed system of $YCrO_3$ having high electrical conductivity and $YAlO_3$ having high electrical insulating properties is free from yielding of subsidiary components on sintering and, after sintering, is mainly composed of $YCrO_3$ and $YAlO_3$ phases, if a matrix is composed of the sintering aids or unavoidable impurities are disregarded. It has also been found that the mixed system exhibits simple reactions and high stability and may be easily adjusted in resistance, such that it can be employed over a broad temperature range of from 300°C to 1100°C.

[0026] According to the process aspect, each of the calcined masses $M^1M^2O_3$ and M^1AlO_3 is pulverized to form a fine powder, preferably having a mean particle size of about 1μm or less. The resulting fine powders are mixed together in a desired proportion, without or preferably with a sintering aid.

[0027] The resultant powdery mixture is formed, e.g., by press-forming, molding, or other known shaping method followed by sintering.

[0028] Each calcination for $M^1M^2O_3$ or M^1AlO_3 is carried out by pre-firing each of a starting raw material mixture with a suitable proportion under the condition that yields synthesized $M^1M^2O_3$ or M^1AlO_3, namely at a sufficient temperature for forming calcined/synthesized mass of each compound. The calcination serves to a better sinterability at a relatively low temperature resulting in a homogeneous product without heterogeneous reaction grades.

[0029] The calcining temperature generally ranges from 1200 to 1400°C so that unreacted residue is minimized and sintering does not proceed in excess so as not to offer difficulty in pulverization.

[0030] The sintering is carried out under the conditions that will sinter the mass-to-be sintered to a sufficient relative density, e.g., 90%, 95% or 98% higher of the theoretical. The sintering temperature does not much depend on the selected elements for M^1, M^2, and generally lies between 1450-1600°C, preferably about 1550°C. Rather the sintering

temperature will be affected by the kind and amount of the sintering aids. The sintering temperature is selected so as to give high stability in the electric properties and a sufficient density of the sintered products.

[0031] According to the preferred embodiments of the present invention, it is generally possible to adjust the resistance values within a desired range according to the proportion of the ingredients (mixing ratios), yet more, with a reduced, controlled resistance change rate in a wider temperature range of 300 to 900°C.

[0032] According to the present invention, a ceramic composition for a thermistor could be produced which is superior in stability at elevated temperature and mechanical strength, and which can be used over a broad temperature range such that it can be used in, for example, a overheating detection device for a catalyst used for cleaning the exhaust gases of automotive vehicles, a hot gas temperature sensor, such as a sensor for recirculated gases in an exhaust gas circulating device, a high temperature measurement device for an area exposed to a higher temperature or a temperature sensor for a variety of furnaces.

[0033] Fig.1 shows an embodiment of a thermistor of the present invention.

Explanation of Numerals

[0034] 1---thermistor element; 2---electrode.

[0035] In the following the present invention will be further elucidated with reference to the preferred embodiments which are not restrictive.

<u>Example 1</u>

[0036] Example 1 of the present invention is now explained.

[0037] Y_2O_3 having a purity of 99.9% or higher and a mean particle size of 1 μm and Cr_2O_3 having a purity of 98.5% or higher and a mean particle size of 1 μm were weighed to a molar ratio of 1:1, mixed by a wet mixing method, dried and calcined (pre-fired) by subsequently maintaining the mixture 1400°C for two hours. The resulting calcined $YCrO_3$ exhibiting high electrical conductivity was pulverized to give powders having a mean particle size of approximately 1 μm.

[0038] On the other hand, Y_2O_3 having a purity of 99.9% or higher and a mean particle size of 1 μm and Al_2O_3 having a purity of 99.9% or higher and a mean particle size of 1 μm were weighted to a molar ratio of 1:1, mixed by a wet mixing method, dried and calcined (pre-fired) by subsequently maintaining the mixture at 1400°C for two hours. The resulting calcined $YAlO_3$ exhibiting high electrical insulating properties was pulverized to give powders having a mean particle size of approximately 1 μm.

[0039] $YCrO_3$ and $YAlO_3$ thus produced were weighed from sample to sample at mixing ratios shown in Table 1 and admixed with 1 wt% of SiO_2 powders having a mean particle size of 0.6 μm. The resulting mass was mixed together by a wet method (ball mill) to give a slurry mixture which was then passed through a sieve through which particles up to about 0.25 mm can pass (200 mesh (JIS)) and subsequently dried. The dried mass was then admixed with a binder composed of 15 wt% of PVB, 10 wt% of DBP, 50 wt% of MEK and 25 wt% of toluene for granulating powders for press molding.

Table 1

Sample No.s	composition		resistance value (KΩ)			β		resistance change rate (%)	
	$YCrO_3$	$YAlO_3$	300°C	650°C	900°C	300-650	650-900	300°C	900°C
1 *	100	0	0.45	0.085	0.06	2520	1510	15[-18]	10[-81]
2	95	5	13.2	0.382	0.130	5350	4670	15[-8]	10[-27]
3	90	10	35.6	0.780	0.240	5770	5104	12[-6]	9[-23]
4	80	20	70.0	0.905	0.285	6570	5000	8[-4]	6[-16]
5	70	30	96.4	1.081	0.327	6790	5180	7[-3]	5[-13]
6	65	35	157	1.824	0.478	6730	5800	10[-5]	8[-17]
7	60	40	296	2.836	0.735	7020	5850	13[-6]	7[-16]
8	55	45	363	3.591	0.952	6980	5750	15[-7]	9[-20]
9	50	50	497	5.100	1.385	6920	5650	15[-7]	8[-18]
10 *	20	80	>30000	57.0	10.3	-	7409	-	-

* marks indicate Comparative Examples

[0040] The resulting powders were charged into a metal mold comprised of two platinum wires, each 0.4 mm in diameter, placed at an interval of 1.2 mm, and were pressed under a pressure of 98 MPa (1000 kg/cm^2), for producing a molded product, 3 mm in diameter and 2 mm in thickness, having two electrode lines of platinum wires, as shown in Fig. 1. The molded product was sintered in ambient air at 1550°C to produce a thermistor element.

[0041] On the thermistor element, thus produced, resistance values in the atmosphere at 300°C, 650°C and 900°C were measured, and values of the temperature gradient constant β were calculated. The results are shown in the columns of the resistance and β. Next, the samples were maintained for 300 hours in the atmosphere at 1000°C and the resistance values thereof at 300°C, 650°C and 900°C before and after the maintenance at 1000°C were measured in order to check the durability. The results are shown in the resistance change rate column in Table 1. The inventive article exhibits high strength as lead wires and can be easily built into temperature sensors. This may presumably be ascribable to the lower sintering temperature.

[0042] In Table 1, β indicates the temperature gradient constant. The temperature gradient constant β, the resistance change rate and the resistance change rate calculated as temperature (converted temperature value derived from the resistance change rate) are defined by the following equations:

$$\beta = \ln(R/R_o)/(1/K-1/K_o)$$

$$\text{resistance change rate} = (R_t - R_o)/R_o \times 100\%$$

where ln indicates common logarithm, and R and R_o indicate resistance values at absolute temperatures K and K_o, respectively. In Table 1, 300-650 and 650 - 900 denote the temperature gradient constants β between 300°C, 650°C and between 650°C and 900°C , respectively.

[0043] R_t denotes the resistance value at an absolute temperature K_t (t=300°C or 900°C) after maintenance at 1000°C for 300 hours.

[0044] The values in the resistance change rate column, shown within square brackets [ ], denote resistance changes before and after the test on durability, as converted into temperatures, and are defined by the following equation:

$$\text{(Resistance change rate, calculated as temperature)} = \beta \times K_o/(\ln(R_t/R_o)\times K_o + \beta)-K_o$$

[0045] It is seen from Table 1 that, by changing the $YCrO_3/YAlO_3$ mixing ratio, the resistance value can be adjusted easily. It is contemplated that no auxiliary components are yielded in the reaction between $YCrO_3$ and $YAlO_3$ and a two-phased mixture is produced after sintering, with the reaction system being simple, so that the resistance value can be adjusted very easily.

[0046] However, if the $YAlO_3$ ratio exceeds 80%, the sinterability is lowered, while the resistance value at 300 °C exceeds 30 megohms(MΩ) and it becomes difficult to measure the resistance value at a temperature range below 300°C, such that the thermistor becomes unsuitable for sensing lower temperatures. Above all, if the resistance value of the thermistor element is set so as to be higher than the insulation resistance between harness lead wires, the thermistor element can hardly be used for detecting the temperature of the exhaust gases of automotive vehicles or as an alarm device for preventing overheating of the catalytic device for cleaning the exhaust gases of the automotive vehicles. The insulation resistances between the lead wires is occasionally lowered to a level of tens of megohms(MΩ). The sample number 10 has an insulating resistance of 30 megohms or higher and hence becomes unusable.

[0047] The resistance change rate of the thermistor element, as measured by the test on durability, was less than 20%, with an exception of sample number 10. Sample number 1 can hardly be used as a thermistor element for a detector device because the value of the constant β thereof is low, and equal to -81°C in terms of the converted temperature value, thus exhibiting poor temperature accuracy.

[0048] Sample number 7 was maintained for ten hours in the atmosphere at 1100°C and resistance values thereof at 300°C and 900°C before and after such maintenance were measured in order to check the resistance change rate. It was found that the change rate was 7% at 300°C, thus indicating the change of -3°C in terms of the converted temperature value. The resistance change rate was 12% at 900°C, thus indicating the change of -26°C in terms of the converted temperature value.

Example 2

[0049] Example 2 is now explained.

[0050] Yb_2O_3 having a purity of 99.9% or higher and a mean particle size of 1.5 μm and Cr_2O_3 having a purity of 98.5% or higher and a mean particle size of 1 μm were weighed to a molar ratio of 1:1, mixed together by a wet mixing method, dried and subsequently calcined maintaining the mixture at 1400°C for two hours. The resulting calcined $YbCrO_3$, exhibiting high electrical conductivity, was pulverized to give powders having a mean particle size of approximately 1 μm.

[0051] On the other hand, Yb_2O_3 having a purity of 99.9% or higher and a mean particle size of 1.5 μm and Al_2O_3 having a purity of 99.9% or higher and a mean particle size of 1 μm were weighed to give a molar ratio of 1:1, mixed together by a wet mixing method, dried and subsequently calcined maintaining the mixture at 1400°C for two hours. The calcined mass was pulverized to give powders having a mean particle size of approximately 1 μm.

[0052] The two kinds of the powders, produced as described above, were weighed to give the composition shown in Table 2, and a thermistor element was produced by the same method as that of Example 1, and the various properties thereof were measured. The results are shown in Table 2. By the way, the respective columns of Tables 2 to 4 have the same meaning as Table 1.

[0053] Sample number 11, represented by $Yb(Cr_{0.60}Al_{0.40})O_3$, has the resistance of 150 kiloohms (KΩ) at 300°C, such that a thermistor element is produced which is capable of being employed in a temperature range from lower temperatures up to higher temperatures.

Table 2

Sample	composition		resistance value (KΩ)			β		resistance change rate(%)	
Nos.	$YbCrO_3$	Yb_2O_3-Al_2O_3	300°C	650°C	900°C	300 -650	650 -900	300°C	900°C
11	60	40	150	1.467	0.450	6990	5120	16[-7]	6[-15]

[0054] The sample number 11 was maintained for ten hours in atmosphere at 1100°C and the resistance values thereof at 300°C and 900°C before and after such maintenance were measured in order to check the resistance change rate. It was found that the change rate at 300°C was 11% which corresponds to a change of -5°C in terms of the converted temperature value. The change rate at 900°C was 7%, which corresponds to a change of -17°C in terms of the converted temperature value.

Example 3

[0055] Example 3 will be now explained. A thermistor element having the composition shown in Table 3 was produced by the same method as in Example 1 except using Er_2O_3 having a purity of 99.9% and a mean particle size of 1

μm. Measurements similar to those in Example 1 were made of the thermistor elements, and the results shown in Table 3 were obtained.

Table 3

Sample Nos.	composition		resistance value (KΩ)			β		resistance change rate(%)	
	$ErCrO_3$	$ErAlO_3$	300°C	650°C	900°C	300-650	650-900	300°C	900°C
12	60	40	250	2.010	0.590	7288	5308	12[-5]	7[-18]

[0056] Sample number 12 was maintained for ten hours in the atmosphere at 1100°C and resistance values at 300°C and 900 °C before and after such maintenance were measured in order to check the resistance change rate. The change rate at 300 °C was 14% which was the change of -6°C in terms of the temperature. The change rate at 900°C was 8% which corresponded to the change of -20°C in terms of the temperature.

EXAMPLE 4

[0057] Example 4 is now explained. Thermistor elements having the compositions shown in Table 4 were produced by the same method as in Example 1 except using Gd_2O_3 having a purity of 99.9% and a mean particle size of 1 μm in place of Y_2O_3. Measurements were made of these elements in the same way as in Example 1, and the results shown in Table 4 were obtained.

[0058] In Table 4, the resistance change rate denotes the resistance change rate before and after the elements were maintained for 300 hours at 1000°C and the corresponding change in terms of the converted temperature values. It is seen that, by setting X in the composition of $(GdCrO_3)_{1-x} \cdot (YAlO_3)_x$ so as to be 0.2 to 0.5, thermistor elements could be produced which exhibited practically optimum resistance values and which exhibited only small resistance change rate value and the resistance change value in terms of the converted temperature value even when the elements were maintained at higher temperatures.

Table 4

Sample Nos.	composition		resistance value (KΩ)			β		resistance change rate (%)	
	$GdCrO_3$	$YAlO_3$	300°C	650°C	900°C	300-650	650-900	300°C	900°C
13	80	20	450	0.530	0.165	6710	5050	15.6[- 7]	3.8[-10]
14	60	40	150	1.650	0.430	6820	5820	18.3[- 8]	4.8[-11]
15	50	50	212	2.950	0.750	6460	5930	22.2[-10]	4.0[-9]

[0059] Sample number 14 was maintained for ten hours in the atmosphere at 1100°C and the resistance values at 300°C and 900°C before and after such maintenance were measured in order to check the resistance change rate. It was found that the change rate at 300°C was 18.4%, which corresponded to the change of -8°C in terms of the converted temperature value. The resistance change rate at 900°C was 44%, which corresponded to the change of -10°C in terms of the converted temperature value.

[0060] Besides the liquid phase forming materials which are essential, the sintering aids may further optionally comprise one or more of the following materials CaO-SiO_2 type compounds, SrO-SiO_2 type compounds, B_2O_3-SiO_2-Al_2O_3 type compounds and B_2O_3-SiO_2 type compounds.

Claims

1. A ceramic composition represented by the formula $(M^1M^2O_3)_{1-x} \cdot (M^1AlO_3)_x$, where

   M^1 is one or more elements selected from the elements belonging to the group 3A excluding La, M^2 is one or more elements selected from the elements belonging to the groups 4A, 5A, 6A, 7A and 8, and 0.8>x>0, preferably x≥ 0.01.

2. The ceramic composition as defined in claim 1 wherein M^1 is one or more elements selected from the group consisting of Y, Sm, Pr, Nd, Dy, Ho, Er, Gd and Yb, and/or M^2 is one or more elements selected from the group consisting of Cr, Ti, Mn, V, Fe and Co.

3. The ceramic composition as defined in claim 1 or 2 wherein x is 0.05 to 0.5, preferably 0.1 to 0.4.

4. The ceramic composition as defined in claim 1, 2 or 3 wherein M^1 is Y or Gd and M^2 is Cr.

5. The ceramic composition as defined in any one of claims 1 to 4 and at least one sintering aid excluding magnesium.

6. The ceramic composition as defined in claim 5 wherein the sintering aid is present in an amount of 0.5 to 10 wt%, preferably 0.8 to 5 wt%.

7. The ceramic composition as defined in claim 5 or 6 wherein the sintering aid is capable of forming a liquid phase in the grain boundary.

8. The ceramic composition as defined in any one of claims 5-7 wherein the sintering aid comprises silica and/or mullite.

9. The ceramic composition as defined in claim 7 or 8 wherein the sintering aid further comprises at least one selected from the group consisting of $CaO\text{-}SiO_2$ type compounds, $SrO\text{-}SiO_2$ type compounds, $B_2O\text{-}SiO_2\text{-}Al_2O_3$ type compounds and $B_2O_3\text{-}SiO_2$ type compounds.

10. The thermistor element having the ceramic composition as defined in any one of the claims 1 to 9 as a main constituent.

11. A process for producing a ceramic composition especially for a thermistor comprising:

   providing $M^1M^2O_3$ and M^1AlO_3, respectively, where M^1 is one or more elements selected from the elements belonging to the group 3A excluding La, M^2 is one or more elements selected from the elements belonging to the groups 4A, 5A, 6A, 7A and 8, and

   then providing a mixture of $(M^1M^2O_3)_{1-x} \cdot (M^1AlO_3)_x$ where $0.8>x>0$, preferably $x\geq0.01$.

12. The process as defined in claim 11, wherein each of said $M^1M^2O_3$ and M^1AlO_3 is produced through calcinating a starting raw material mixture to form a calcined mass.

13. The process as defined in claim 11 or 12 wherein M^1 is one or more elements selected from the group consisting of Y, Sm, Pr, Nd, Dy, Ho, Er, Gd and Yb and M^2 is one or more elements selected from the group consisting of Cr, Ti, Mn, V, Fe and Co.

14. The process as defined in claim 11, 12 or 13 wherein x is 0.05 to 0.5, preferably 0.1 to 0.4.

15. The process as defined in any one of claims 11-14 wherein M^1 is Y or Gd and M^2 is Cr.

16. The process as defined in any one of claims 11 to 15 and providing at least one sintering aid excluding magnesium.

17. The process as defined in one of claims 12 to 16, wherein each of said calcined masses is pulverised to form a fine powder.

18. The process as defined in claim one of claims 12 to 17 wherein the calcination is carried out approximately at 1200-1400°C, preferably about 1400°C.

19. A process for producing a thermistor element, comprising the steps of the process as defined in any one of claims 11-18, and further comprising sintering said mixture.

20. The process as defined in claim 19, wherein a sintering aid is admixed to said pulverised powders.

21. The process as defined in claim 19 or 20 wherein the sintering is carried out at a temperature approximately of 1450 to 1600°C, preferably about 1550°C.

22. The process as defined in one of claims 16 to 18 or 20 and 21 wherein the sintering aid comprises silica and/or mullite.

23. The process as defined in one of claims 16 to 18, or 20 to 22 wherein the sintering aid further comprises at least one compound selected from the group consisting of CaO-SiO_3 type compounds, SrO-SiO_2 type compounds, B_2O_2-SiO_2-Al_2O_3 type compounds and B_2O_2-SiO_2 type compounds.

Patentansprüche

1. Keramikverbindung, dargestellt durch die Formel $(M^1M^2O_3)_{1-x} * (M^1AlO_3)_x$, wobei

   es sich bei M^1 um ein oder mehrere Elemente handelt, die aus den Elementen ausgewählt werden, welche zur Gruppe 3A gehören, wobei La ausgeschlossen ist, und wobei es sich bei M^2 um ein oder mehrere Elemente handelt, die aus den Elementen ausgewählt werden, die zu den Gruppen 4A, 5A, 6A, 7A und 8 gehören, und $0{,}8>x>0$, vorzugsweise $x \geq 0{,}01$ ist.

2. Keramikverbindung nach Anspruch 1, wobei es sich bei M^1 um ein oder mehrere Elemente handelt, die aus der Gruppe bestehend aus Y, Sm, Pr, Nd, Dy, Ho, Er, Gd und Yb ausgewählt werden, und/oder wobei es sich bei M^2 um ein oder mehrere Elemente handelt, die aus der Gruppe bestehend aus Cr, Ti, Mn, V, Fe und Co ausgewählt werden.

3. Keramikverbindung nach Anspruch 1 oder 2, wobei x gleich 0,05 bis 0,5, vorzugsweise jedoch 0,1 bis 0,4 ist.

4. Keramikverbindung nach Anspruch 1, 2 oder 3, wobei M^1 gleich Y oder Gd und M^2 gleich Cr ist.

5. Keramikverbindung nach einem der Ansprüche 1 bis 4 mit mindestens einer Sinterhilfe außer Magnesium.

6. Keramikverbindung nach Anspruch 5, wobei die Sinterhilfe in einer Menge von 0,5 bis 10 Gewichtsprozent, vorzugsweise in einer Menge von 0,8 bis 5 Gewichtsprozent vorhanden ist.

7. Keramikverbindung nach Anspruch 5 oder 6, wobei die Sinterhilfe in der Lage ist, eine Flüssigkeitsphase in der Korngrenze zu bilden.

8. Keramikverbindung nach einem der Ansprüche 5 - 7, wobei die Sinterhilfe Siliciumdioxid und/oder Mullit umfaßt.

9. Keramikverbindung nach Anspruch 7 oder 8, wobei die Sinterhilfe weiters mindestens eine Verbindung ausgewählt aus der Gruppe bestehend aus CaO-SiO_2-artigen Verbindungen, SrO-SiO_2-artigen Verbindungen, B_2O-SiO_2-Al_2O_3-artigen Verbindungen und B_2O_3-SiO_2-artigen Verbindungen umfaßt.

10. Heißleiterelement mit der Keramikverbindung nach einem der Ansprüche 1 bis 9 als Hauptbestandteil.

11. Verfahren zur Herstellung einer Keramikverbindung besonders für einen Heißleiter, umfassend:

    das Schaffen von $M^1M^2O_3$ beziehungsweise M^1AlO_3, wobei es sich bei M^1 um ein oder mehrere Elemente handelt, die von den Elementen ausgewählt werden, welche zur Gruppe 3A gehören, wobei La ausgeschlossen ist, und wobei es sich bei M^2 um ein oder mehrere Elemente handelt, die aus den Elementen ausgewählt werden, welche zu den Gruppen 4A, 5A, 6A, 7A und 8 gehören, und

    danach das Schaffen einer Mischung aus $(M^1M^2O_3)_{1-x} * (M^1AlO_3)_x$, wobei $0{,}8>x>0$, vorzugsweise $x \geq 0{,}01$ ist.

12. Verfahren nach Anspruch 11, wobei sowohl $M^1M^2O_3$ als auch M^1AlO_3 durch Kalzinierung einer anfänglichen Rohmaterialmischung zur Bildung einer kalzinierten Masse erzeugt werden.

13. Verfahren nach Anspruch 11 oder 12, wobei es sich bei M^1 um ein oder mehrere Elemente handelt, die aus der Gruppe bestehend aus Y, Sm, Pr, Nd, Dy, Ho, Er, Gd und Yb ausgewählt werden, und wobei es sich bei M^2 um ein

oder mehrere Elemente handelt, die aus der Gruppe bestehend aus Cr, Ti, Mn, V, Fe und Co ausgewählt werden.

14. Verfahren nach Anspruch 11, 12 oder 13, wobei x gleich 0,05 bis 0,5, vorzugsweise 0,1 bis 0,4 ist.

15. Verfahren nach einem der Ansprüche 11 - 14, wobei es sich bei M^1 um Y oder Gd und bei M^2 um Cr handelt.

16. Verfahren nach einem der Ansprüche 11 bis 15 und das Schaffen mindestens einer Sinterhilfe außer Magnesium.

17. Verfahren nach einem der Ansprüche 12 bis 16, wobei jede der kalzinierten Massen pulverisiert wird, um ein feines Pulver zu erhalten.

18. Verfahren nach einem der Ansprüche 12 bis 17, wobei die Kalzinierung bei etwa 1200 - 1400 °C, vorzugsweise bei etwa 1400 °C ausgeführt wird.

19. Verfahren zur Herstellung eines Heißleiterelements, umfassend die Schritte des Verfahrens nach einem der Ansprüche 11 - 18, und weiters umfassend das Sintern der Mischung.

20. Verfahren nach Anspruch 19, wobei eine Sinterhilfe den pulverisierten Pulvern beigemischt wird.

21. Verfahren nach Anspruch 19 oder 20, wobei das Sintern bei einer Temperatur durchgeführt wird, die etwa 1450 bis 1600 °C, vorzugsweise etwa 1550 °C beträgt.

22. Verfahren nach einem der Ansprüche 16 bis 18 oder 20 und 21, wobei die Sinterhilfe Siliciumdioxid und/oder Mullit umfaßt.

23. Verfahren nach einem der Ansprüche 16 bis 18, oder 20 bis 22, wobei die Sinterhilfe weiters mindestens eine Verbindung umfaßt, die aus der Gruppe bestehend aus CaO-SiO_3-artigen Verbindungen, SrO-SiO_2-artigen Verbindungen, B_2O_2-SiO_2-Al_2O_3-artigen Verbindungen und B_2O_2-SiO_2-artigen Verbindungen ausgewählt wird.

Revendications

1. Composition céramique représentée par la formule $(M^1M^2O_3)_{1-x} \cdot (M^1AlO_3)x$ où M^1 est un ou plusieurs éléments choisis par des éléments appartenant au groupe 3A à l'exclusion du La, M^2 est un ou plusieurs éléments choisis parmi les éléments appartenant aux groupes 4A, 5A, 6A, 7A et 8, et $0,8>x>0$, avantageusement $x\geq0,01$.

2. Composition céramique selon la revendication 1, dans laquelle M^1 est un ou plusieurs éléments choisis dans le groupe constitué de Y, Sm, Pr, Nd, Dy, Ho, Er, Gd et Yb et/ou M^2 est un ou plusieurs éléments choisis dans le groupe constitué de Cr, Ti, Mn, V, Fe et Co.

3. Composition céramique selon la revendication 1 ou 2, dans laquelle $\underline{x}$ est de 0,05 à 0,5, avantageusement de 0,1 à 0,4.

4. Composition céramique selon la revendication 1, 2 ou 3, dans laquelle M^1 est Y ou Gd et M^2 est Cr.

5. Composition céramique selon l'une quelconque des revendications 1 à 4 et au moins un auxiliaire de frittage à l'exclusion du magnésium.

6. Composition céramique selon la revendication 5, dans laquelle l'auxiliaire de frittage est présent en quantité de 0,5 à 10 % en poids, avantageusement 0,8 à 5 % en poids.

7. Composition céramique selon la revendication 5 ou 6, dans laquelle l'auxiliaire de frittage est capable de former une phase liquide dans le joint des grains.

8. Composition céramique selon l'une quelconque des revendications 5-7, dans laquelle l'auxiliaire de frittage comprend de la silice et/ou de la mullite.

9. Composition céramique selon la revendication 7 ou 8, dans laquelle l'auxiliaire de frittage comprend en outre au moins un auxiliaire choisi dans le groupe constitué de composés du type CaO-SiO_2, de composés du type SrO-

SiO_2, de composés du type B_2O-SiO_2-Al_2O_3 et de composés du type B_2O_3-SiO_2.

10. Elément à thermistance ayant la composition céramique selon l'une quelconque des revendications 1 à 9 en tant que constituant principal.

11. Procédé pour la production d'une composition céramique en particulier pour une thermistance, comprenant :

l'utilisation de $M^1M^2O_3$ et M^1AlO_3, respectivement, où M^1 est un ou plusieurs éléments choisis parmi les éléments appartenant au groupe 3A à l'exclusion du La, M^2 est un ou plusieurs éléments choisis parmi les éléments appartenant aux groupes 4A, 5A, 6A, 7A et 8, et
on utilise ensuite un mélange de $(M^1M^2O_3)_{1-x} \cdot (M^1AlO_3)_x$ où 0,8>x>0, avantageusement x≥0,01.

12. Procédé selon la revendication 11, dans lequel chacun desdits $M^1M^2O_3$ et M^1AlO_3 est produit par calcination d'un mélange de matières premières de départ pour former une masse calcinée.

13. Procédé selon la revendication 11 ou 12, dans lequel M^1 est un ou plusieurs éléments choisis dans le groupe constitué de Y, Sm, Pr, Nd, Dy, Ho, Er, Gd et Yb et M^2 est un ou plusieurs éléments choisis dans le groupe constitué de Cr, Ti, Mn, V, Fe et Co.

14. Procédé selon la revendication 11, 12 ou 13, dans lequel $\underline{x}$ est de 0,05 à 0,5, avantageusement de 0,1 à 0,4.

15. Procédé selon l'une quelconque des revendications 11-14, dans lequel M^1 est Y ou Gd et M^2 est Cr.

16. Procédé selon l'une quelconque des revendications 11 à 15 et utilisant au moins un auxiliaire de frittage à l'exclusion du magnésium.

17. Procédé selon l'une des revendications 12 à 16, dans lequel chacune desdites masses calcinées est pulvérisée pour former une poudre fine.

18. Procédé selon l'une des revendications 12 à 17, dans lequel la calcination est exécutée à environ 1200-1400°C, avantageusement environ 1400°C.

19. Procédé pour la production d'un élément à thermistance, comprenant les étapes du procédé selon l'une quelconque des revendications 11-18, et comprenant en outre le frittage dudit mélange.

20. Procédé selon la revendication 19, dans lequel un auxiliaire de frittage est mélangé auxdites poudres pulvérisées.

21. Procédé selon la revendication 19 ou 20, dans lequel le frittage est exécuté à une température d'environ 1450 à 1600°C, avantageusement d'environ 1550°C,

22. Procédé selon l'une des revendications 16 à 18 ou 20 et 21, dans lequel l'auxiliaire de frittage comprend de la silice et/ou de la mullite.

23. Procédé selon l'une des revendications 16 à 18, ou 20 à 22, dans lequel l'auxiliaire de frittage comprend en outre au moins un composé choisi dans le groupe constitué de composés du type CaO-SiO_3, de composés du type SrO-SiO_2, de composés du type B_2O_2-SiO_2-Al_2O_3 et de composés du type B_2O_2-SiO_2.

F I G. 1